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DISTRIBUTION OF TRANSITION ELEMENTS IN CRUSTAL METABASIC IGNEOUS ROCKS

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ABSTRACT

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The study of transition elements (Ti, V, Ni, Cr, Co, Cu, Zn, Fe, Mn) and Mg in metabasic crustal igneous rocks (amphibolites, granulites, eclogites) suggests that the distribution is not specially affected by medium- and high-grade metamorphism. In some cases, anomalously low contents of Ni, Cr and Cu may be more likely related to a previous low-grade metamorphic event. It seems that the fractionation of these elements is related to initial magmatic assemblages. It is demonstrated from the elements studied that most of the metabasites have an affinity with extrusive oceanic tholeiites and continental intrusive tholeiites. Thus, the subsequent high-grade metamorphism may be related either to the emplacement of basaltic magmas in the lower continental crust or to the underthrusting of the oceanic crust.

INTRODUCTION

The ancient magmatic rocks are one of the keys to understanding the past geotectonic history of the crust. Unfortunately, these rocks are generally strongly altered by metamorphic processes and their original chemical composition may have changed. Various workers (Pearce et al., 1975; Winchester and Floyd, 1976, etc.) have tried to avoid this difficulty by analysing those trace elements considered to be relatively immobile during metamorphic processes (Y, Zr, Nb, Ti, P, REE). The aim of this paper is to contribute to such studies by analysing in medium- and high-grade crustal metabasites (amphibolites, granulites and eclogites) the transition elements which are also considered to be stable during metamorphism (Jolly and Smith, 1972; Holland and Lambert, 1975; Bridgwater and Collerson, 1976). The advantage of such elements (Ti, V, Ni, Cr, Co, Cu, Zn, Mn) is that each of them has a specific af-

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finity for a given mineralogical phase (e.g., Ni for olivine). The behaviour of the transition elements during their successive mineralogical transformations and the comparison with the behaviour and contents of such elements in recent volcanic rocks may help to characterize their original magmatic type and geotectonic setting.

For this purpose, we have gathered data published by various authors as well as our own results on the metabasic rocks of the French Massif Central. The study was restricted to basic rocks whose magmatic origin is clearly demonstrated by these authors. These basic terms are chosen using the classification of volcanic rocks: SI > 35 for tholeiitic basalts, DI < 35 for alkali basalts, $SiO_2 < 56\%$ for basic andesites and basalts related to orogenic zones (Taylor, 1969; Maury, 1976; Andriambololona, 1978; Andriambololona and Dupuy, 1978).

BEHAVIOUR OF TRANSITION ELEMENTS IN METABASIC ROCKS

The transition element data are plotted in Fig. 1 against the FeO*/MgO ratio (FeO* = total Fe as FeO) (Miyashiro and Shido, 1975) for some representative examples of amphibolites, granulites and eclogites. All the series show characteristic trends of volcanic rocks (Miyashiro and Shido, 1975). Cr, Ni and Co decrease more or less steadily with the FeO*/MgO ratio. Ti and V generally increase, displaying a trend characteristic of tholeiitic series (Miyashiro and Shido, 1975). However, in some localities (Odenwald amphibolites: Klemm and Weber-Diefenbach, 1971; Madras granulites: Sen and Ray, 1971), Ti remains constant or slightly decreases as in modern volcanics of orogenic zones. In some sequences which have suffered different grades of metamorphism, the behaviour of transition elements is not disturbed (e.g., amphibolites and granulites of the Strona Valley, D.R. Andriambololona, unpublished data, 1978; amphibolites of Greenland found both in amphibolite and granulite facies, Rivalenti and Rossi, 1975).

In spite of these similarities, some differences remain: (1) for a given value of the differentiation index, the transition-element contents are more scattered in metabasites than in volcanic rocks, especially for Cu and Zn; (2) low Ni and/or Cr contents (up to 5 ppm) in many metabasites (eclogites of Bohemia: Fediukova and Dudek, 1977; amphibolites of Sardinia: Ricci and Sabatini, 1973, etc.); (3) depletion in Cu, especially in amphibolites and granulites as already pointed by Andriambololona et al. (1977) and Dupuy et al. (1977) (amphibolites of the Strona Valley; D.R. Andriambololona, unpublished data, 1978; amphibolites of Brazil: Roeser and Müller, 1977; granulites of Bournac: Leyreloup et al., 1977). These contents are close to those found for oceanic gabbros (Table I).

The averaged contents are reported in Tables I and II for metabasic rocks, subdivised according to the previous considerations.

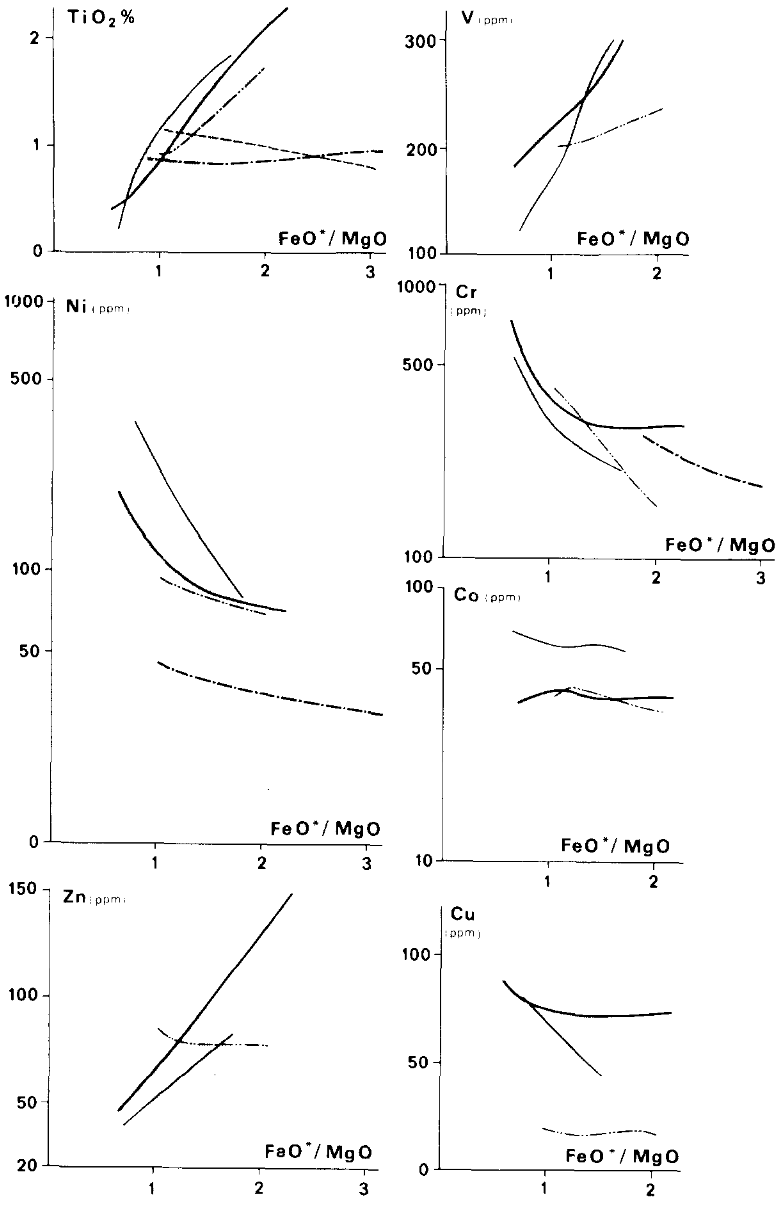

Fig. 1. Variation of the transition elements vs. the FeO*/MgO ratio in some representative metabasic rocks suites.

Amphibolites: Acebuches (Dupuy et al., 1979) (———); and Odenwald (Klemm and Weber-Diefenbach, 1971) (— . —).

Granulites: Bournac (Leyreloup et al., 1977) (— . . —); and Madras (Sen and Ray, 1971) (— — —).

Eclogites: Hohen Tauern (Richter, 1973) (▬▬).

Shaded area: abyssal tholeiite fields after Andriambololona (1978).

TABLE I

Average contents for tholeiitic metabasites, abyssal tholeiites and oceanic gabbros

	n	TiO_2	*n*	V	*n*	Cr	*n*	MnO
Amphibolites:								
PI	4	0.56 (0.33)	2	162 (53)	4	723 (573)	4	0.16 (0.03)
PII	1	0.96	1	188	1	960	1	0.18
BII	22	1.16 (0.33)	16	237 (55)	22	316 (102)	22	0.17 (0.04)
BIII	19	1.34 (0.32)	10	283 (73)	19	300 (132)	19	0.19 (0.05)
Granulites:								
PI	4	0.70 (0.19)	4	201 (37)	4	483 (274)	4	0.14 (0.02)
PII	4	1.28 (0.58)	4	226 (50)	4	364 (185)	4	0.13 (0.04)
BII	9	1.15 (0.48)	9	202 (16)	9	372 (144)	9	0.13 (0.04)
BIII	2	1.98 (1.36)	2	255 (98)	2	269 (64)	2	0.15 (0.02)
Eclogites:								
PI	7	0.45 (0.4)	7	164 (33)	7	540 (197)	7	0.10 (0.04)
PII	16	0.53 (0.35)	3	235 (7)	16	457 (201)	16	0.12 (0.07)
BII	11	0.87 (0.43)	6	250 (45)	11	342 (124)	11	0.14 (0.04)
BIII	10	0.86 (0.13)	7	226 (18)	10	325 (55)	10	0.19 (0.08)
Olivine abyssal tholeiites:								
PI	6	0.69 (0.18)	2	176 (36)	6	1,022 (413)	6	0.16 (0.01)
PII	14	0.85 (0.41)	14	204 (34)	14	541 (154)	14	0.16 (0.02)
BII	12	1.14 (0.22)	12	245 (32)	12	399 (129)	12	0.16 (0.02)
BIII	14	1.53 (0.19)	14	292 (37)	14	256 (113)	14	0.18 (0.02)
Plagioclase abyssal tholeiites:								
PI	4	0.78 (0.20)		—	4	393 (122)	4	0.15 (0.02)
PII	5	0.75 (0.40)	5	195 (20)	5	270 (114)	5	0.12 (0.04)
BII	7	0.99 (0.23)	7	218 (29)	7	296 (142)	7	0.16 (0.05)
BIII	11	1.24 (0.20)	11	290 (14)	11	253 (70)	11	0.15 (0.03)
Oceanic gabbros:								
PI	15	0.33 (0.01)	15	153 (10)	15	1,028 (507)	15	0.13 (0.02)
BII	4	0.53 (0.17)	4	223 (19)	4	210 (50)	4	0.14 (0.01)

Data are taken for:
(A) Amphibolites, from Knauer et al. (1974); Rivalenti and Rossi (1975); Van Calsteren (1978); Dupuy et al. (1979); unpublished data for French Massif Central (C. Nicollet, 1978), and Strona Valley rocks (D.R. Andriambololona, 1978).
(B) Granulites, from Leyreloup et al. (1977) unpublished data of Strona Valley rocks (D.R. Andriambololona, 1978).
(C) Eclogites, from Bryhni et al. (1969); Richter (1973); Raheim (1976); Van Calsteren (1978); unpublished data for French Massif Central rocks (C. Nicollet, 1978).
For comparison various averaged values are reported for Recent tholeiites compiled by Andriambololona (1978). The subdivision in each rock type is established as follows:
PI: IS > 45, R = Mg/(Mg + Fe) > 0.72; PII: IS > 45, 0.72 ⩾ R ⩾ 0.66.
BI: 45 ⩾ IS ⩾ 35, R > 0.72; BII: 45 ⩾ IS ⩾ 35, 0.72 ⩾ R ⩾ 0.66; BIII: 45 ⩾ IS ⩾ 35, 0.66 > R ⩾ 0.60; BIV: 45 ⩾ IS ⩾ 35, 0.60 > R.
n = number of samples in the four groups; ( ) = standard deviation.
*Total Fe as FeO.

n	FeO*	*n*	Co	*n*	Ni	*n*	Cu	*n*	Zn	Ti/V	Mg/Ni
4	7.96 (1.66)	3	54 (15)	2	214 (234)	2	37 (35)	2	59 (21)	21 (7)	313 (243)
1	8.42	1	52	1	358	1	13	1	58	30	154
22	9.05 (1.75)	17	59 (8)	20	121 (57)	16	58 (55)	16	67 (18)	29 (2)	389 (45)
19	9.22 (2.42)	12	62 (14)	17	111 (87)	10	42 (56)	10	78 (29)	28 (3)	421 (81)
4	8.43 (2.65)	4	37 (12)	4	104 (44)	4	17 (4)	4	69 (17)	21 (3)	554 (122)
4	10.93 (1.53)	4	70 (12)	4	191 (117)	4	22 (16)	4	95 (42)	34 (9)	319 (102)
9	9.07 (1.18)	9	49 (7)	9	102 (54)	9	17 (1)	9	84 (9)	34 (5)	473 (84)
2	9.84 (1.63)	2	58 (25)	2	106 (51)	2	24 (10)	2	136 (31)	46 (25)	429 (153)
7	6.80 (0.68)	7	51 (13)	7	463 (215)	7	74 (22)	4	49 (13)	16 (6)	142 (28)
16	7.53 (1.18)	16	40 (25)	16	143 (73)	16	84 (59)	14	53 (10)	14 (2)	407 (62)
11	8.51 (1.34)	11	46 (22)	11	99 (45)	10	73 (36)	9	64 (21)	21 (3)	503 (71)
10	9.90 (1.25)	10	48 (18)	9	92 (41)	4	67 (38)	2	92 (47)	23 (1)	535 (84)
6	8.56 (0.55)	7	57 (2)	6	423 (216)	6	91 (8)	2	63 (10)	—	122 (119)
14	8.79 (0.63)	14	56 (12)	14	216 (48)	14	91 (27)	14	64 (4)	25 (13)	277 (69)
12	8.86 (0.25)	12	53 (16)	12	168 (69)	12	82 (14)	12	67 (4)	28 (6)	321 (134)
14	9.99 (1.07)	14	48 (15)	14	122 (51)	14	76 (18)	14	80 (14)	31 (5)	394 (169)
4	8.01 (1.25)		—	4	144 (22)	4	66 (18)		—	—	403 (68)
5	6.80 (1.67)	5	34 (13)	5	102 (23)	5	73 (25)	5	56 (7)	23 (12)	449 (149)
7	8.29 (0.90)	7	35 (6)	7	108 (37)	7	67 (5)	7	61 (12)	27 (7)	443 (164)
11	9.02 (0.74)	11	42 (4)	11	96 (20)	11	62 (19)			26 (4)	472 (104)
15	5.70 (0.19)	15	41 (16)	15	219 (30)	15	64 (6)			13 (1)	277 (67)
4	6.63 (0.85)	4	39 (19)	4	105 (35)	4	18 (4)			14 (5)	476 (93)

COMPARISON BETWEEN METABASIC ROCKS AND CORRESPONDING NON-METAMORPHIC VOLCANICS

Main components factorial analysis applying to the first series of transition elements has been carried out both for basalts and metabasic rocks and reported graphically in Fig. 2. The following results were obtained from the program printout: the lower right-hand side of this figure is a plot of loadings on factors F_1 and F_2. This figure divides the elements in two groups: Ni, Cr and Mg, and Zn, Ti and Fe; in each group, these elements display a strong positive correlation indicating a close similarity in their behaviour; the eigenvalues F_1 and F_2 comprise a total of 67% of the information available for separating the magma types; the eigenvectors show that these two functions are:

$$F_1 = -0.037\,x'_{\mathrm{MnO}} + 0.519\,x'_{\mathrm{MgO}} + 0.018\,x'_{\mathrm{TiO_2}} + 0.158\,x'_{\mathrm{Fe_2O_3}} + 0.508\,x'_{\mathrm{Cr}} + 0.384\,x'_{\mathrm{Co}} + 0.518\,x'_{\mathrm{Ni}} + 0.171\,x'_{\mathrm{Cu}} - 0.016\,x'_{\mathrm{Zn}}$$

$$F_2 = -0.376\,x'_{\mathrm{MnO}} + 0.047\,x'_{\mathrm{MgO}} - 0.555\,x'_{\mathrm{TiO_2}} - 0.517\,x'_{\mathrm{Fe_2O_3}} + 0.128\,x'_{\mathrm{Cr}} - 0.065\,x'_{\mathrm{Co}} + 0.020\,x'_{\mathrm{Ni}} - 0.032\,x'_{\mathrm{Cu}} - 0.501\,x'_{\mathrm{Zn}}$$

TABLE II

Averaged contents of calc-alkali amphibolites (Klemm and Weber-Diefenbach, 1971; Weber-Diefenbach, 1976) and volcanic rocks (Andriambololona, 1978).

	n	TiO_2 (%)	*n*	Cr (ppm)	*n*	MnO (%)	*n*	FeO* (%)	*n*	Co (ppm)	*n*	Ni (ppm)	Ni/Co	Mg/Ni
Amphibolites:														
B	53	1.03 (0.33)	40	137 (126)	53	0.23 (0.09)	53	12.3 (3.10)	40	35 (26)	53	44 (30)	1.26 (0.19)	807 (81)
AB	7	1.02 (0.17)	5	98 (105)	7	0.25 (0.11)	7	9.69 (0.7)	5	38 (19)	7	25 (10)	0.66 (0.18)	1,247 (268)
Continental margin:														
B	13	1.29 (0.46)	13	143 (76)	13	0.19 (0.18)	13	8.01 (1.53)	13	34 (3)	13	72 (66)	2.12 (1.95)	450 (424)
AB	21	1.10 (0.14)	17	199 (36)	21	0.13 (0.01)	21	7.26 (0.30)	10	30 (3)	17	70 (29)	2.33 (0.99)	488 (314)
Island arc:														
B	43	0.97 (0.27)	43	69 (173)	43	0.18 (0.06)	43	9.22 (1.40)	43	38 (12)	43	34 (80)	0.89 (2.12)	943 (2,241)
AB	43	0.86 (0.08)	10	38 (81)	53	0.17 (0.04)	53	8.02 (0.61)	8	33 (8)	10	16 (14)	0.61 (0.44)	1,611 (1,085)

Basalt (B) and basic andesites (AB) subdivision: B: $SiO_2 < 53\%$; AB: $53\% \leqslant SiO_2 < 56\%$.
n = number of samples in the two groups.
*Total Fe as FeO.

TABLE III

Mean and standard deviations obtained for 93 selected basic rocks

	MnO (%)	MgO (%)	TiO_2 (%)	Fe_2O_3 (%)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)
$\bar{x}$	0.166	9.45	1.65	11.22	419	54	219	79	82
s	0.024	4.10	0.91	1.85	389	17	268	40.2	25

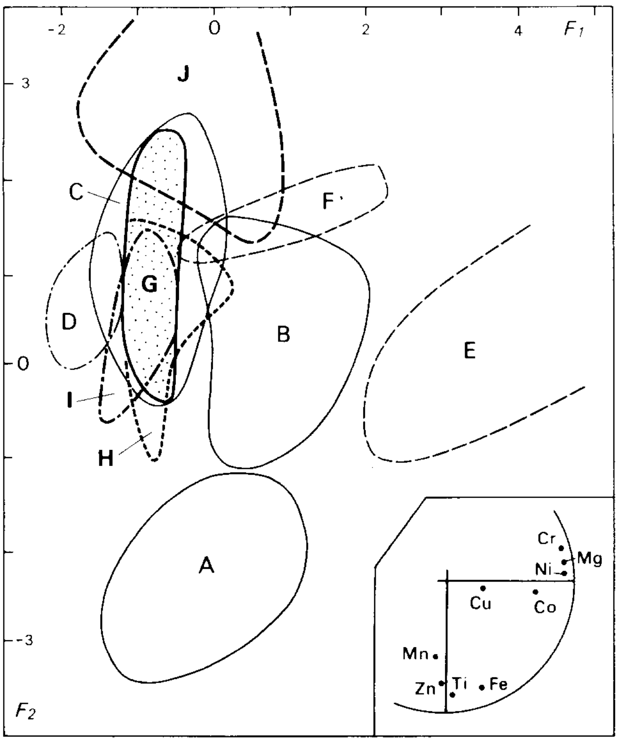

Fig. 2. Plot of factors score F_1 and F_2 for volcanic rocks (picrites and basalts) and metabasites (data from Table I). $F_1 + F_2$ account for 67% of the total variance with factor 1 contributing 37%.
A = alkali basalts; B = extrusive continental and island tholeiites; C = abyssal tholeiites; D = orogenic volcanic rocks; E = picrites of continental and island tholeiites; F = picrites of abyssal tholeiites; G = eclogites; H = granulites; I = amphibolites; and J = picrites of metabasites.

with $x' = (x - \bar{x})/s$; $\bar{x}$ and s are respectively mean and standard deviations obtained for 93 selected basic rocks and reported in Table III.

Fig. 2 shows that the transition elements discriminate the different volcanic rocks (Andriambololona, 1978). The three types of metabasites cluster in the abyssal tholeiites field. This kind of representation accounts for the different

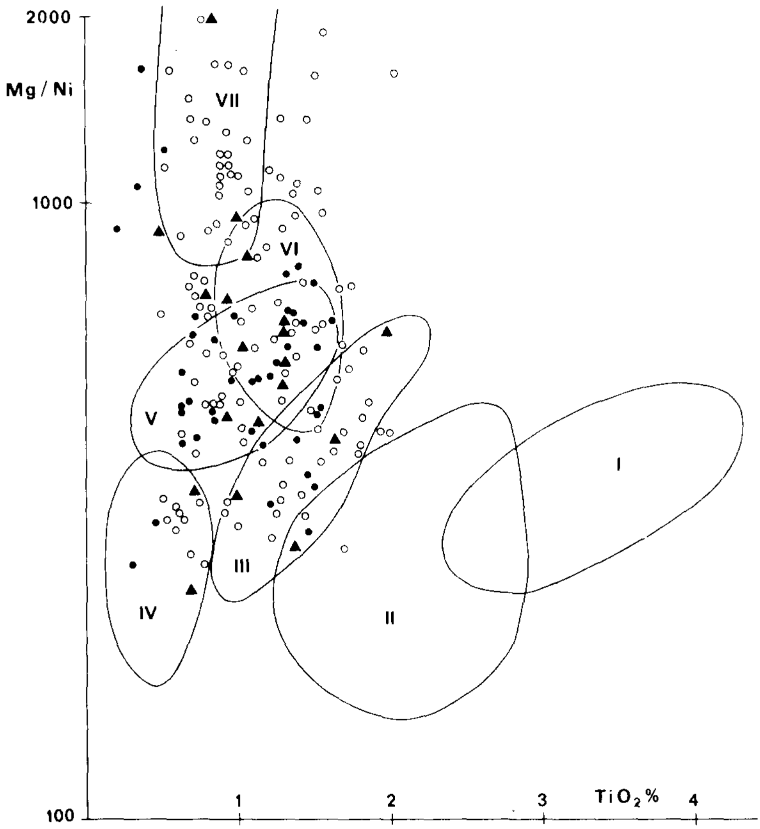

Fig. 3. Mg/Ni ratio vs. TiO_2.
Open circles: amphibolites (Van de Kamp, 1969; Prato, 1970; Klemm and Weber-Diefenbach, 1971; Knauer et al., 1974; Rivalenti and Rossi, 1975; Weber-Diefenbach, 1976; Dupuy et al., 1979; unpublished data for Rouergue, French Massif Central: C. Nicollet (1978); and Strona Valley: D.R. Andriambololona (1978).
Triangles = granulites (Leyreloup et al., 1977; unpublished data for French Massif Central: Marchand; and Strona Valley: Andriambololona (1978).
Full circles = eclogites (Bryhni et al. 1969; Ernst, 1977: Matthes and Seidel, 1977; Miller, 1970; Råheim, 1976; Richter, 1973; unpublished data for Rouergue: Nicollet (1978).
Continuous lines define the fields occupied by alkali and transitional basalt (*I*); extrusive continental tholeiites (*II*); olivine abyssal tholeiites and oceanic island tholeiites (*III*); oceanic gabbros and olivine normative dolerites (*IV*); plagioclase abyssal tholeiites, quartz-normative dolerites and Skaergaard gabbro (Wager and Mitchell, 1951 (*V*); continental margin calc-alkali rocks (*VI*); and island arc tholeiites and calc-alkali rocks (*VII*).

transition elements but remains restrictive because of the scarcity of the samples in which all transition elements are available. In consequence, another graph, Mg/Ni vs. TiO_2 using only three elements, but allowing us to consider increased numbers of samples, is presented in Fig. 3. TiO_2 displays large variations and specially discriminates between alkali and tholeiitic affinities and the Mg/Ni ratio may control the olivine fractionation (Gunn, 1971). Moreover, this graph discriminates between intrusive and extrusive rocks. It shows that most of the metabasites cluster in the field of oceanic tholeiites, gabbros and dolerites except some examples which lie in the field of orogenic volcanic rocks (Odenwald amphibolites: Klemm and Weber-Diefenbach, 1971; Tyrol amphibolites: Weber-Diefenbach, 1976). None of the series studied falls in the field of the continental tholeiites nor in that of alkali basalts. However, Ricci and Sabatini (1978) have shown (by analysing Y, Zr, Nb, La and Ce) the alkaline affinity of the Sardinian amphibolites. This affinity is corroborated by high Ti, V and Ti/V contents despite low Ni and Cr contents.

DISCUSSION

The similarity in behaviour of the transition elements in the metabasites and in the volcanic rocks, suggests that the magmatic fractionation trend is preserved during the medium- and high-grade metamorphic events. In consequence, the distribution of the transition elements is more likely related to the mineralogical phases of the original basalt than to those of the corresponding metabasite as claimed by Fediukova and Dudek (1977). Although olivine and spinel are generally absent in metabasites, the rapid decrease of Cr and Ni during the earliest step of differentiation suggests a fractionation due to olivine and spinel. These two minerals are the only ones with partition coefficients high enough to deplete Ni and Cr rapidly during the differentiation (Frey et al. 1974). We believe thus that metamorphic transformations do not necessarily change the chemical composition of medium- and high-grade basic rocks, as was suggested by Forbes (1965) and Bryhni et al. (1969).

In this hypothesis, the very low Cr, Ni and Cu contents of some metabasites could be explained by some event earlier than the medium- or high-grade metamorphism. However, Andriambololona and Chikhaoui (in prep.) have shown that Cr, Ni and Cu may be depleted during low-grade metamorphism. Furthermore, Miyashiro et al. (1969), Thompson (1973), Bonatti et al. (1975), Pamic, (1974), and C.G. Engel and Fisher (1975) argued that the low Cu content of oceanic gabbros is due to seawater alteration. Such events may affect the rocks before the high-grade metamorphism. Low Cr and Ni contents of Bohemian eclogites (Fediukova and Dudek, 1977) and Cu depletions of some eclogites of the French Massif Central (C. Nicollet, unpublished data, 1978) showing gabbroic characters (honeycomb structure and low TiO_2 content) may be related to such processes.

Most of these metabasites have an affinity with oceanic tholeiites. Some of them may have a continental affinity (granulites of Bournac: A. Leyreloup, pers. commun., 1978); or quartz dolerites: Råheim, 1976). Only a few amphibolites have a calc-alkaline affinity. These observations are in agreement with the conclusions of Matthes (1978) for the German eclogites but in disagreement with the conclusions of Forbes (1965) who believes that the scarcity of alkali eclogites is only due to the alkali loss during metamorphism.

CONCLUSIONS

This study suggests that the distribution and the behaviour of the transition elements in metabasites is not specially affected by medium- and high-grade metamorphism. The depletion of Ni, Cr and Cu in some localities may be more likely the result of a previous low-grade event. In metabasites, the fractionation of transition elements is related to the initial magmatic mineralogic phases of the original basalt. Thus, these elements appear very useful in the determination of the original geochemical affinity of the metabasic rocks. However, it is very difficult to separate, with transition elements alone, the extrusive oceanic tholeiites and the intrusive continental tholeiites. The two rock types with tholeiitic affinity are the most widespread among the metabasites. This feature appears logical by reference to the respective proportions of the actual magmatic type (A.E.J. Engel et al., 1965). The subsequent high-grade metamorphism may be related either to the emplacement of basaltic magmas in the lower continental crust (Griffin and Heier, 1973), or to the underthrusting of the oceanic crust (Miyashiro, 1972).

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